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(54) Enamel composition

(57) An enamel composition comprising by weight (A) 25-90 parts of frit particles, (B) 10-75 parts of platelet pigment particles, and (C) at least 2 parts of silver particles, all per 100 parts in total of (A) and (B), is abrasion resistant and can mimic the colour of gold. The composition may be used in a carrier medium as a decorating ink.

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ENAMEL COMPOSITION

This invention relates to an enamel composition, a decorating ink containing it, a transfer bearing a decoration comprising the enamel composition, a method of decorating a surface using the decorating ink or the transfer, and an article bearing the enamel composition fired on its surface.

Enamel compositions are used to decorate surfaces by application thereto and usually thereafter firing. The present invention concerns particularly the decoration of ceramic or glass surfaces. Enamel compositions for such use comprise a frit and a pigment. The pigment provides the decorative effect, for instance colour, and the frit (which is a glass flux composition) binds the pigment to the surface and provides abrasion resistance. There are problems, however, when the pigment is of

the type termed herein platelet pigments. These pigments comprise platelets, usually of mica, which are coated with metal oxide and/or metal. The visual effect of the pigments is described in such terms as pearl lustre, pearlescent, iridescent, and having an interference colour effect. Enamel compositions based on these pigments give decorations which are not as abrasion resistant as is desired, for instance to household scouring materials.

Although some compositions or techniques using these pigments are said to afford stability against abrasion, the need for abrasion resistance remains . A new way of increasing abrasion resistance has been discovered, affording a new enamel composition. In addition, in a preferred embodiment, the new enamel composition gives a decoration which mimics the golden colour of gold decorations and hence can be used in their place. Gold and its compounds are rare and expensive. Gold decorating inks are difficult to apply, and gold decorations are generally less resistant to abrasion and chemical attack than other decorations. In addition, gold decorating inks tend to sink into any underlying enamel composition and lose their colour. Further, enamel compositions applied over a burnish gold decorating ink tend to form a disrupted surface, known as "frizzle", on firing. Furthermore, continuous gold films tend to spark in microwave ovens. Hence, a replacement for gold is beneficial.

European patent specification 313281A2 discloses a pigment comprising a ceramic scaly substrate characterized in that metal dots or alloy dots

are formed on the surfaces of said ceramic scaly substrate in a ratio of 0.05 to 95% of the total surface area of said ceramic scaly substrate.

The present invention provides an enamel composition comprising by weight:

(A) 25-90 parts of frit particles;

(B) 10-75 parts of platelet pigment particles; and

(C) at least 2 parts of silver particles;

per 100 parts in total of (A) and (B).

The invention provides also a decorating ink comprising the composition and a carrier medium.

The invention also provides a transfer comprising a transfer paper bearing a releasable decoration comprising the enamel composition.

The invention provides also a method of preparing the transfer, which method comprises applying the decorating ink to the transfer paper to form a decoration releasable from the paper.

The invention also provides a method of decorating the surface of an article, which method comprising applying the decorating ink to the surface to form the decoration, or transferring to the surface a decoration from the transfer.

The invention provides also an article bearing the enamel composition fired on its surface.

It has been found that incorporating silver particles into an enamel composition comprising frit particles and platelet pigment particles increases the abrasion resistance. Thus, one can obtain a higher abrasion resistance. Alternatively one can obtain a given level of abrasion resistance while employing less frit, which enhances the visual effect.

The present enamel which mimics the golden colour of gold decorations without being based on gold, termed herein the "gold effect" enamel, has better abrasion and chemical resistance than does a gold decoration. The enamel is microwave safe. The enamel is more versatile than gold decorations since it can be present over or under other enamels.

It can be seen that the present silver particles are distinguished from any silver coating on the platelets which accordingly forms part of the pigment, *eg* the silver dots on the platelets discussed in the European specification mentioned above. It is much easier to incorporate the present silver into the enamel composition, *eg* by simple mixing, than it is to apply any silver coating on the platelets.

The present pigment particles are of known type, see for instance the European specification mentioned above, which describes the pigment as being a

ceramic scaly material, US specification 5032429, which refers to mica platelets coated with a thin light-impermeable or light-permeable coating of a metallic oxide and describes mica as possessing a scaly, plate-like crystal structure, and US specification 5022923, which refers to mica flakes coated with metal oxides. The platelet pigments described in any of these specifications can be employed.

The platelets generally have an average thickness from 0.05 to 0.50 micron, usually from 0.3 to 0.5 micron. Their average length is generally from 3 to 200 microns, usually from 3 to 60 microns. The platelets can be of molybdenum disulphide but are generally of mica. The mica can be natural, such as muscovite, biotite or phlogopite, or synthetic. Mica can be considered as formed of $(Si, Al)_2O_5$ layers that are coupled through Al-, Mg-Fe atoms and additionally contain alkali metal and alkaline earth metal ions; the chemical composition of micas is variable. The platelets are coated with metal oxide and/or metal. There can be one or more coatings. The platelets can be coated all over with a coating of metal or metal oxide. There can be an all-over coating of metal over an all-over coating of metal oxide.

The metal oxide is usually one or more of TiO_2, Fe_2O_3, ZrO_2, Al_2O_3, ZnO, Sb_2O_3, SiO_2, CuO, NiO, CoO, Cr_2O_3 and SnO_2, preferably TiO_2 and/or Fe_2O_3, and especially TiO_2.

A coating of metal (including metal alloy) dots, *eg* of Au, Ag, Cu, Pd or Co, as described in the European specification mentioned above, can be present.

A metal oxide coating can bear a further coating, which is of a colouring film, *eg* of chromium oxide, iron oxide, iron blue pigment or carbon black.

The pigment can have a top coating of tin dioxide and/or cerium dioxide.

Specific pigments which are suitable are of the "Iriodin" range available from Merck.

The pigment can be conventional, as can the frit. The frit can be chosen depending on the intended use. It can comprise PbO, SiO_2, B_2O_3, Al_2O_3 and Na_2O. Alternatively, it can be lead-free.

In a preferred embodiment, the particle size of the frit is lower than normal. Preferably the D_{90} of the frit is at most 8 microns and especially lies in the range 2-5 microns. The D_{90} value means that 90% of the total volume of particles present have a size below this value, where the size is the diameter of a sphere of the same volume, as measured by the Fraunhofer scattering of light model. Particle sizes referred to herein are as measured on a Malvern Mastersizer X machine after 15 minutes ultrasonic treatment to break up agglomerates. This preferred particle size results in the fired decoration appearing less granular and more continuous, like a metallic film. It is thought that this occurs by the small size of frit allowing the platelets to become aligned.

The silver particles can be silver flake. Silver powder is preferred, since it is cheaper than silver flake.

The enamel composition comprises the frit particles, platelet pigment particles and silver particles. The composition contains 25-90 parts of the frit particles, and 10-75 parts of the platelet pigment particles, per 100 parts in total of these 2 ingredients. Parts in this specification are by weight unless otherwise indicated. Preferably the weight of the frit particles is 25-70, especially 45-60, parts per 100 parts in total of the frit particles and platelet pigment particles.

The amount of platelet pigment particles depends on the visual effect, such as the strength of colour, desired. The amount is 10-75, preferably 30-75, especially 40-55, parts per 100 parts in total of the frit particles and platelet pigment particles.

The amount of silver particles is usually up to 40 parts per 100 parts in total of the frit particles and platelet pigment particles. Lower amounts of silver particles are preferred since silver is relatively rare and hence relatively expensive, and usually the desired abrasion resistance can be obtained from the lower amounts. Usually the amount of silver particles is at least 5 parts per 100 parts in total of the frit particles and platelet pigment particles. The amount is preferably 5-30, especially 10-15, parts per 100 parts in total of the frit particles and platelet pigment particles.

The enamel composition can contain a plurality of different platelet pigment particles. In this way, a range of coloured decorating inks can be obtained.

The enamel composition can contain also other pigment. In this way, the colour can be altered dramatically. Usually, the amount of the other pigment is 2-15, preferably 2-10, especially 2-5, parts per 100 parts in total of (A) and (B). The lower amounts are usually preferred since the higher amounts may result in a decrease in the lustre of the enamel.

In a preferred embodiment, the other pigment is dark-coloured, say having a CIElab lightness coordinate of at most 40, where white has a value of 100 and black a value of 0. This other pigment is preferably employed such that the composition is golden coloured, say of CIElab coordinates:lightness 68-76, chroma 26-36 and hue 80-86. It has been found that the use of such dark coloured pigments surprisingly enables a decoration to be obtained which mimics the golden colour of gold decorations, and hence can be used in their place. The dark coloured pigments can give an "old gold" or burnished gold appearance in this way. Copper chrome black (DCMA reference number 13-38-9) is a suitable other pigment for this purpose.

The enamel composition is usually employed in the form of a decorating ink comprising the composition and a carrier medium. The enamel composition and the decorating ink can be made and used in conventional ways. They can be made by mixing their ingredients, preferably by low-shear mixing such

as by using a dough mixer. Grinding, however, should be kept to a minimum since it can cause the platelet pigment particles to break up, reducing the lustre of the fired composition. It is not necessary to form the enamel composition and then admix this with a carrier medium, as long as the ink comprises the ingredients of the enamel composition in their desired proportions and the carrier medium. For instance, one can disperse, for instance by light triple roll milling, the ingredients of the enamel composition in the carrier medium to obtain the ink.

Conventional carrier media can be employed. When the decorating ink is applied by printing, the carrier medium is a printing medium. The ratio of the total weight of (A), (B) and (C) to the weight of the carrier medium is usually 1:1.5-5. In the case of a screen printing medium, this ratio is usually 1:1.5-4, preferably 1:2-3.

The decorating ink can be applied directly to the surface of an article, *eg* a ceramic, glass or enamelled steel article, to be decorated to form the decoration. Alternatively, the surface can be decorated by means of a transfer, by transferring to the surface a decoration comprising the enamel composition from the transfer.

The transfer can be conventional in itself. It comprises a transfer paper bearing a releasable decoration comprising the enamel composition. The transfer can be prepared in the conventional way, by applying the decorating ink to transfer paper to form a decoration releasable from the paper. This can be done by applying the decorating ink onto a release layer (*eg* of a water-soluble gum or a

heat-releasable wax) on transfer paper. On top, there is usually a covercoat to protect the transfer and hold the decoration during its transfer to the surface to be decorated.

The decorating ink can be applied to the transfer paper or surface to be decorated in the conventional way. Application can be by printing, *eg* screen printing. The screen opening of the printing screen is preferably at least 10 microns larger than the maximum particle size of the platelet pigment particles to ensure that a sufficient thickness of ink is deposited. Alternatively, application can be by painting.

The decoration can be transferred from a transfer to the surface to be decorated in the conventional way. The transfer can be a water slide transfer, in which case it can be employed by soaking it in water to release a covercoat bearing the decoration and this covercoat bearing the decoration applied to the surface. Alternatively, the transfer can be a heat release transfer, in which case it can be employed by contacting it with a holding surface so that, because of a difference in temperature between the holding surface and the transfer paper, the decoration is released from the transfer paper and held by the holding surface, after which the decoration so held is contacted with the surface to be decorated and, because of a difference in temperature between the surface to be decorated and the holding surface, the decoration is released from the holding surface and adheres to the surface to be decorated.

The surface to be decorated is preferably ceramic or glass. Preferably the surface is of an article of china, porcelain, earthenware, glass or enamelled steel (in which case the surface can be considered as glass).

After application to the surface, directly or via a transfer, the decoration is usually fired. The firing can be conventional. It is usually at a temperature of at least 450°C. The temperature is usually at most 1000°C since the platelet pigment particles tend to decompose, losing their lustre, above this temperature. The optimum temperature depends on the surface. For ceramic surfaces, the temperature is preferably 750-900°C, while for glass surfaces it is preferably 500-750°C.

The present enamel composition gives a very attractive lustrous decoration. In a preferred embodiment, the decoration after firing is golden coloured, say having CIElab coordinates: lightness 55-90 (preferably 64-78), hue 60-90 (preferably 70-82) and chroma 5-52 (preferably 7-49). The present decoration can be on top of or below a different enamel. This versatility is particularly useful in the case of the gold effect enamel in view of the difficulties mentioned above of employing real gold inks on top of or below an enamel composition.

The invention is illustrated by the following Examples

EXAMPLES 1 and 2

and COMPARATIVE EXAMPLES 1-6

Method of Preparation of Decorating Inks:

The ink components set out in Table 1 are combined and mixed gently. The mixture is then triple roll milled lightly, to create a homogeneous dispersion. The ink is then printed through a 77T polyester screen, which has a screen opening size at least 10 microns larger than the maximum size of the platelet pigment. The ink is printed onto Twincal II transfer (decal) paper (which bears a water-soluble gum release layer) produced by Brittains (TR) Ltd, of England, using a Dek 245 screen printer. The ink is allowed to dry at room temperature for 6 hours before coating with OPL 164 covercoat resin produced by Cookson Matthey Ceramics plc, of England. A transfer is thus obtained.

For comparison with real gold formulations, the same procedure, except for using the polyester screen noted, was employed to make a transfer from the burnished gold formulation gmc 11045 from Cookson Matthey Ceramics plc, of England (90T screen, Comparative Example 4) and a transfer from the bright gold formulation gbc 10123/s from Cookson Matthey Ceramics plc, of England (120T screen, Comparative Example 5).

The decoration is transferred from the transfer to the surface of porcelain by soaking the transfer in water to release the covercoat bearing the

decoration and applying this covercoat to the surface. The decoration is fired using the following cycle: ramp from room temperature up to 820°C over 30 minutes; hold at 820°C for a dwell time of 10 minutes; cool back to room temperature (25°C) over 20 minutes. In further comparison, the self burnishing gold formulation gdc 11214 from Cookson Matthey Ceramics plc, of England was painted using a brush onto porcelain, and fired in the same way (Comparative Example 6).

Table 1

	Frit	Platelet Pigment	Silver	Other Pigment	Medium
Comparative Example 1	A 5.00g	C 5.00g	-	-	F 20.00g
Comparative Example 2	B 5.00g	C 5.00g	-	-	F 20.00g
Example 1	B 4.50g	C 4.50g	D 1.00g	-	F 25.00g
Comparative Example 3	B 4.85g	C 4.85g	-	E 0.30g	F 25.00g
Example 2	B 4.38g	C 4.07g	D 1.25g	E 0.30g	F 25.00g

A is 2C186, unleaded frit, supplied by Cookson Matthey Ceramics, England.

B is 2C186, unleaded frit, that has been vibro-milled to a particle size distribution with a D_{90} of 4.82 μm, supplied by Cookson Matthey Ceramics, England.

C is Iriodin 306, supplied by Merck Ltd, England, and is a micacious pigment, coated with a layer of TiO_2 in the form of anatase, with a particle size range of 10-60 µm.

D is CAP 9 silver powder, supplied by Johnson Matthey PLC, England.

E is 1E2002 copper chrome black pigment, supplied by Cookson Matthey Ceramics, England.

F is a 80709 Screen Printing Oil, supplied by Degussa, Germany, and is an acrylic resin in 1,3,5 trimethyl benzene and iso-propyl benzene.

Abrasion Resistance Tests

Abrasion resistance tests were carried out using a REL Abrasion Tester. The fired porcelain is placed in the equipment so that the decoration lies directly below the abrasive head. A felt pad, coated with approximately 0.25g carborundum paste, is placed in the head and a 1kg weight is placed on top of the head. The abrasive head is rubbed over the decoration for 500 strokes. Each stroke is a double movement where the pad travels back and forward across the decoration. The decoration is examined after every 100 strokes (except where indicated in the Table below) for the degree of wear, which is assessed by comparing the sample with a set of standard gold decorations which have undergone different amounts of

7. A composition according to any one of the preceding claims wherein the frit particles have a D_{90} particle size, as defined herein, of at most 8 microns.

8. A decorating ink comprising a composition claimed in any one of the preceding claims and a carrier medium.

9. A transfer comprising a transfer paper bearing a releasable decoration comprising an enamel composition claimed in any one of claims 1-7.

10. A method of preparing a transfer claimed in claim 9, which method comprises applying to transfer paper a decorating ink claimed in claim 8 to form a decoration releasable from the paper.

11. A method of decorating the surface of an article, which method comprises applying to the surface a decorating ink claimed in claim 8 to form the decoration, or transferring to the surface a decoration from a transfer claimed in claim 9.

12. A method according to claim 11 wherein the decoration is thereafter fired.

13. A method according to claim 12 wherein the surface is of a ceramic, glass or enamelled steel article.